Molecular Selective Adsorption on a Multibilayer-coated Piezoelectric Crystal

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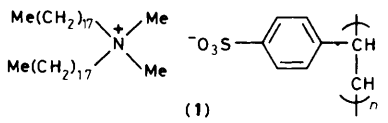
The molecular selective adsorption and penetration of hydrophobic alcohols or cholesterol into synthetic multibilayer matrices depending on their chemical structures were detected by observing the frequency change of a bilayer-coated piezoelectric crystal in an aqueous solution.

Recently, we have reported that various bitter substances[1] and odorants[2] adsorb specifically on a synthetic multibilayer-coated piezoelectric crystal in aqueous and gas phases. Good correlations were observed between partition coefficients of bitter or odor substances to lipid bilayers and the bitter taste or olfactory threshold values in humans, respectively. However, the structure of bitter substances or odorants is extremely diverse and it is difficult to find the molecular recognition mechanism by lipid bilayers in chemical structure levels.

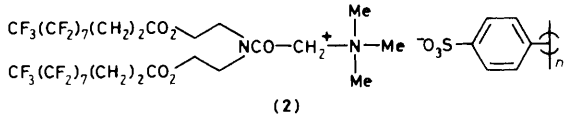
We now report a piezoelectric study of the molecular-selective adsorption behaviour of simple model compounds (eleven hydrophobic alcohols) on synthetic lipid multibilayer films dependent on their chemical structures. The structures of polyion complex type multibilayer-immobilized films are illustrated. Linear long chain, branched, or sterically bulky aliphatic alcohols, aromatic alcohols, cholesterol, and perfluorinated alcohols were selected as additives in aqueous solution.

Polymeric bilayer-forming amphiphiles (**1**)—(**4**) prepared previously[1—3] were cast from chloroform on both sides of the silver electrode deposited piezoelectric crystal (9 MHz, AT cut, 8 × 8 mm). These films were 0.5 ± 0.2 μm thick (20 ± 5 μg). Each amphiphile formed extended multibilayer structures (3—4 nm thick) parallel to the film plane in a polyion complex with poly(styrene sulphonate).[1—3] A multibilayer-immobilized film was chosen because of the long term stability of multibilayers on a crystal in an aqueous solution. Hydrophobic alcohols were injected as ethanolic solutions (5—50 μl) into stirred distilled water (10 ml). The frequency reverted to the original value on immersing the crystal in fresh distilled water owing to desorption. Partition coefficients (P) to the lipid bilayer from the aqueous phase were calculated by dividing the amount adsorbed in the lipid matrix by the concentration in the aqueous phase (Table 1). The frequency of the crystal was observed to be affected mainly by the amount adsorbed and not to respond to changes in viscosity or density of the coating and the aqueous solution.[4]

Some alcohols adsorbed rapidly (within 30 s) only near the surface and did not penetrate into the multibilayer matrix on the crystal since $P < 2000$ (Type A behaviour). However,



(1)



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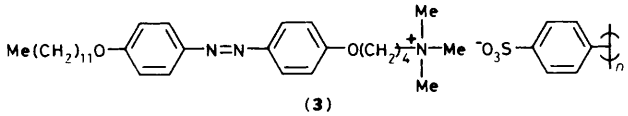

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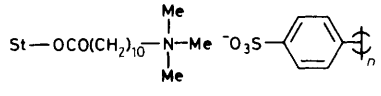
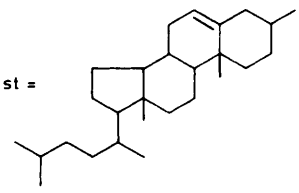
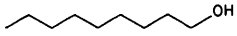
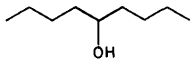
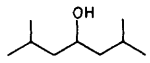
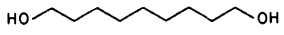
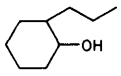
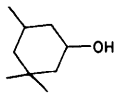
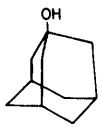
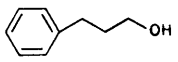
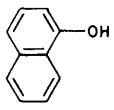




(4)

Table 1. Partition coefficients of hydrophobic alcohols to lipid multibilayer matrices on a piezoelectric crystal.[a]

Additives	None	Polystyrene	Lipid bilayer (1) (dialkyl)	(2) (perfluorinated)	(3) (chromophore-containing)	(4) (cholesteric)
	30	600	6000	1900	1500	800
	40	100	200	500	300	200
	50	100	100	60	100	50
	20	20	500	900	300	300
	20	80	300	50	200	100
	30	100	200	60	100	50
	40	100	50	60	50	50
	10	100	100	100	100	40
	50	100	900	200	300	300
St—OH	50	100	50	8200	300	15000
$CF_3(CF_2)_7$—OH	20	50	14000	16000	13000	10000

[a] Averages from five experiments (experimental error ±5%).

others adsorbed slowly (10—30 min) and penetrated deeply into the multibilayer matrix where $P > 5000$ (Type B behaviour).

When uncoated crystal or a crystal coated with amorphous polystyrene film was employed, partition coefficients were very small ($P < 100$) and were independent of the chemical structures of the hydrophobic alcohols. n-Nonanol adsorbed specifically and penetrated deeply into dialkyl amphiphile bilayers (**1**) (Type B) compared with the surface adsorption (Type A) to perfluorinated (**2**), chromophore-containing (**3**), and cholesteric (**4**) amphiphiles. Branched aliphatic alcohols or aromatic alcohols showed small partition coefficients with Type A adsorption to all lipid bilayers on the crystal.

Cholesterol adsorbed specifically with penetration into the cholesteric multibilayer matrix on the crystal (Type B) and hardly adsorbed on the dialkyl amphiphile bilayers (Type A). The perfluorinated alcohol adsorbed with penetration into all lipid bilayers irrespective of the lipid structure ($P > 10000$), and the partition coefficient for the perfluorinated bilayer was larger than that for other lipid matrices.

Thus, the linear long chain alcohol, cholesterol, and perfluorinated alcohol adsorbed selectively into the dialkyl amphiphile bilayers, the cholesteric bilayers, and the perfluorinated bilayers, respectively. A branched or sterically bulky alcohol cannot penetrate into lipid bilayer matrices irrespective of their chemical structures. This is the first example of the selective molecular recognition of the synthetic bilayer membranes. These results can be extended to solve the molecular-level mechanism of a biological chemoreception in lipid bilayers.

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